Extrusion Coating

This invention relates to a process for extrusion
coating a substrate with a polyethylene composition as
well as to the extruded coated structures themselves.
More particularly, the invention concerns the use of
certain bimodal single site polyethylenes in extrusion
coating.

Low density polyethylene (LDPE), conventionally made
in a high pressure radical process, preferably in an
autoclave reactor, has been used in extrusion coating
for many years. In extrusion coating, the polymer resin
is melted and formed into thin hot film, which is
normally coated onto a moving, flat substrate such as
paper, paperboard, metal foil, or plastic film. The
coated substrate then passes between a set of counter-
rotating rollers, which press the coating onto the
substrate to ensure complete contact and adhesion.

Polymers used in extrusion coating need to possess
certain properties to make them useful as coatings. For
example, the coatings should provide adequate moisture
barriers and exhibit good sealing properties; they must
also possess the requisite mechanical properties and hot
tack. In this regard LDPE's do not possess the ideal
mechanical properties required by an extrusion coating
since they lack the necessary toughness and abuse
resistance. It is known therefore to blend LDPE's with
other polymer grades to improve mechanical properties.

Hence LDPE has previously been combined with higher
density polyethylenes, e.g. medium or high density
polyethylene or linear low density polyethylenes to
improve mechanical properties. For example, a small
amount of LDPE (5 to 30 wt%) can be added to LLDPE to
improve processability in an extrusion coating
composition. However, when the content of LDPE
increases in the composition, then the beneficial

properties of the linear polymer, e.g. environmental
stress cracking resistance, barrier properties, sealing
properties, are soon diluted or lost. On the other hand
if the LDPE content is too low then the blend may not
have sufficient processability. The problem with such
low LDPE content blends is that whilst they have better
processability than an LLDPE alone, they may not be
extrudable or drawn down at high take-off rates. There
is therefore a trade off between good mechanical
properties and good processability.

Linear low density polyethylene (LLDPE) and ultra
low density polyethylene (ULDPE) extrusion compositions,
conventionally made using Ziegler-Natta catalysis offer
improved mechanical properties but again are difficult
to process due to lack of extrudability.

There remains a need therefore to devise further
polyethylene polymer compositions suitable for extrusion
coating which provide both good mechanical and
processing properties.

WO01/62847 proposes a solution to this problem by
using a bimodal polyethylene composition made using a
single site catalyst in a multistage process. The
composition can be used as an extrusion coating as such
or mixed with minor amounts of LDPE prior to extrusion.
The polymer produced is preferably a bimodal
ethylene/butene copolymer with butene being used in both
loop and gas phase stages of a two stage process.

Whilst the polymers described in WO01/62847 have
acceptable seal initiation temperatures and relatively
broad sealing windows their hot tack strength is
limited. In this regard, it is known that hexene-
ethylene copolymers provide superior sealing properties
than butene-ethylene copolymers and that an octene-
ethylene copolymer provides superior properties to a
hexene-ethylene copolymer.

However, the use of higher alpha-olefin comonomers,
i.e. C_6 or greater alpha-olefins, increases the cost of

the polymer product and, generally, the efficiency of
comonomer incorporation decreases as the carbon number
of the comonomer increases, i.e. hexene is less
efficiently incorporated than butene and octene is less
5   efficiently incorporated than hexene, etc. The skilled
artisan is reluctant therefore to include higher
comonomers.

We have now surprisingly found that by incorporating
two different alpha-olefin comonomers a multimodal, e.g.
10 bimodal, polyethylene composition ideal for extrusion
coating may be produced which has superior sealing
properties and hot tack properties to the polyethylenes
produced using either of the comonomers as the sole
comonomer.

15 Thus viewed from one aspect the invention provides
an extrusion coated substrate said coating comprising a
polyethylene produced by polymerization catalysed by a
single site catalyst and comprising as comonomers to
ethylene at least two C_{4-12} alpha olefins, preferably at
20 least two alpha olefins selected from but-1-ene, hex-1-
ene, 4-methyl-pent-1-ene, hept-1-ene, oct-1-ene, and
dec-1-ene, particularly but-1-ene and hex-1-ene.

Viewed from another aspect the invention provides
the use of a polyethylene produced by polymerization
25 catalysed by a single site catalyst and comprising as
comonomers to ethylene at least two C_{4-12} alpha olefins,
preferably at least two alpha olefins selected from but-
1-ene, hex-1-ene, 4-methyl-pent-1-ene, hept-1-ene, oct-
1-ene, and dec-1-ene, particularly but-1-ene and hex-1-
30 ene in extrusion coating or for the formation of cast
films.

In many cases, the seal which is formed between the
surfaces to be sealed is put under load while it is
still warm. This means that the hot-tack properties of
35 the polyethylene are crucial to ensure a strong seal is
formed even before cooling. All extrusion coatings have
a window within which sealing may occur, i.e. in which

the extrudate becomes partly molten. Traditionally this sealing window has been rather narrow meaning that temperature control during the heat sealing process is critical. The polymers of the invention allow a broader

5 sealing window so allowing the sealing operation to take place at lower temperature and ensuring that temperature control during heat sealing is less important. By operating at lower temperature there are the benefits that the article to be sealed is not exposed to high

10 temperature and any other component of the extrusion coating which may not be involved in sealing are also not exposed to high temperature. There are also economic advantages since lower temperatures are of course cheaper to generate and maintain.

15   The polyethylene of the extrusion coating of the invention is typically a mixture of two or more polyethylenes, e.g. produced by blending or by two-or-more stage polymerization reactions. The constituent polyethylenes may be homopolymers, copolymers,

20 terpolymers or polymers of four or more comonomers; preferably however at least one polymer is a terpolymer or at least two polymers are copolymers, in particular in which one monomer, the major component, is ethylene and one or two comonomers, the minor components, are C_4

25 and/or C_6 alpha-olefins.

It is especially preferred that the polymer be prepared in a two or more stage polymerization in which in an earlier stage the lower alpha-olefin comonomer (e.g. but-1-ene) is incorporated and in which in a later

30 stage the higher alpha-olefin comonomer (hex-1-ene) is incorporated. Nonetheless, it is within the scope of the invention to produce the polymer in a two stage polymerization reaction in which an ethylene homopolymer is produced in the first stage and an ethylene

35 terpolymer is produced in the second stage or vice versa or in which an ethylene copolymer with the higher alpha-olefin comonomer is produced in the first stage

and an ethylene copolymer with the lower alpha-olefin comonomer is produced in the second stage. Likewise, an ethylene copolymer may be produced in the first stage and an ethylene terpolymer in the second stage and vice

5 versa. It is also possible to employ a prepolymerisation stage as is well known in the art.

In a most preferred embodiment the polyethylene is formed from a mixture of an ethylene/but-1-ene copolymer (lower molecular weight component) preferably made in

10 the slurry phase and an ethylene/hex-1-ene copolymer (higher molecular weight component) preferably made in the gas phase.

The expression "homopolymer" of ethylene used herein refers to a polyethylene that consists substantially,

15 i.e. at least 98% by weight, preferably at least 99% by weight, more preferably at least 99.5% by weight, most preferably at least 99.8% by weight, of ethylene units.

The ethylene polymers of the invention are produced using a so-called single site catalyst, e.g. a catalyst

20 comprising a metal coordinated by one or more η-bonding ligands. Such η-bonded metals are normally referred to as metallocenes and the metals are typically Zr, Hf or Ti, especially Zr or Hf. The η-bonding ligand is typically an η^5-cyclic ligand, i.e. a homo or

25 heterocyclic cyclopentadienyl group optionally with fused or pendant substituents. Such metallocene catalysts have been widely described in the scientific and patent literature for about twenty years. Such metallocene catalysts are frequently used with catalyst

30 activators or co-catalysts, e.g. alumoxanes such as methylaluminoxane, again as widely described in the literature.

The polymer used in the extrusion coatings of the invention preferably is multimodal, e.g. bimodal, i.e.

35 its molecular weight profile does not comprise a single peak but instead comprises the combination of two or

more peaks (which may or may not be distinguishable) centred about different average molecular weights as a result of the fact that the polymer comprises two or more separately produced components. In this

5 embodiment, a higher molecular weight component preferably corresponds to a copolymer (or terpolymer etc.) of the higher alpha-olefin comonomer and a lower molecular weight component preferably corresponds to an ethylene homopolymer or a copolymer (or terpolymer etc.)

10 of the lower alpha-olefin comonomer. Such bimodal ethylene polymers may be prepared for example by two or more stage polymerization or by the use of two or more different polymerization catalysts in a one stage polymerization. Preferably however they are produced in

15 a two-stage polymerization using the same catalyst, e.g. a metallocene catalyst, in particular a slurry polymerization in a loop reactor followed by a gas phase polymerization in a gas phase reactor. A loop reactor - gas phase reactor system has been developed by Borealis

20 A/S, Denmark and is known as BORSTAR® technology.

Preferably, the lower molecular weight polymer fraction is produced in a continuously operating loop reactor where ethylene is polymerized in the presence of a polymerization catalyst as stated above and a chain

25 transfer agent such as hydrogen. The diluent is typically an inert aliphatic hydrocarbon, preferably isobutane or propane. A C_4 to C_{12} alpha-olefin comonomer is preferably added to control the density of the lower molecular weight copolymer fraction.

30 Preferably, the hydrogen concentration is selected so that the lower molecular weight copolymer fraction has the desired melt flow rate. More preferably, the molar ratio of hydrogen to ethylene is between 0.1 and 1.5 mol/kmol, most preferably, between 0.2 and 1.0

35 mol/kmol.

In the case the target density of the lower molecular weight copolymer fraction exceeds 955 kg/m³, it

is advantageous to operate the loop reactor using propane diluent in so called supercritical conditions where the operating temperature exceeds the critical temperature of the reaction mixture and the operating

5 pressure exceeds the critical pressure of the reaction mixture. A preferred range of temperature is then from 90 to 110°C and the range of pressures is from 50 to 80 bar.

The slurry is intermittently or continuously removed

10 from the loop reactor and transferred to a separation unit where at least the chain transfer agents (e.g. hydrogen) are separated from the polymer. The polymer containing the active catalyst is then introduced into a gas phase reactor where the polymerization proceeds in

15 the presence of additional ethylene, comonomer(s) and optionally chain transfer agent to produce the higher molecular weight copolymer fraction. The polymer is intermittently or continuously withdrawn from the gas phase reactor and the remaining hydrocarbons are

20 separated from the polymer. The polymer collected from the gas phase reactor is the polyethylene composition of the invention.

The conditions in the gas phase reactor are selected so that the ethylene polymer has the desired properties.

25 Preferably, the temperature in the reactor is between 70 and 100°C and the pressure is between 10 to 40 bar. The hydrogen to ethylene molar ratio ranges from preferably 0 to 1 mol/kmol, more preferably 0 to 0.5 mol/kmol and the alpha-olefin comonomer to ethylene molar ratio

30 ranges from preferably 1 to 100 mol/kmol, more preferably 5 to 50 mol/kmol and most preferably 5 to 30 mol/kmol.

The extrusion coating process may be carried out using conventional extrusion coating techniques. Hence,

35 the polymer obtained from the polymerisation process is fed, typically in the form of pellets, optionally containing additives, to an extruding device. From the

extruder the polymer melt is passed through a flat die
to the substrate to be coated. Due to the distance
between the die lip and the nip, the molten plastic is
oxidised in the air for a short period, usually leading

5   to an improved adhesion between the coating and the
substrate. The coated substrate is cooled on a chill
roll, after which it is passed to edge trimmers and
wound up. The width of the line may vary between, for
example, 500 to 1500 mm, e.g. 800 to 1100 mm, with a

10 line speed of up to 1000 m/min, for instance 300 to 800
m/min. The temperature of the polymer melt is typically
between 275 and 330°C.

     The multimodal polyethylene composition of the
invention can be extruded onto the substrate as a

15 monolayer coating or as one layer in coextrusion. In
either of these case it is possible to use the
multimodal polyethylene composition as such or to blend
the multimodal polyethylene composition with other
polymers, especially LDPE so that the blend contains

20 from 0 to 50%, preferably from 10 to 40% and in
particular 15 to 35% of LDPE, based on the weight of the
final blend. Blending can occur in a post reactor
treatment or just prior to the extrusion in the coating
process.

25   In a multilayer extrusion coating, the other layers
may comprise any polymer resin having the desired
properties and processabiiity. Examples of such
polymers include: barrier layer PA (polyamide) and EVA;
polar copolymers of ethylene, such as copolymers of

30 ethylene and vinyl alcohol or copolymers of ethylene and
an acrylate monomer; adhesive layers, e.g. ionomers,
copolymers of ethylene and ethyl acrylate, etc; HDPE for
stiffness; polypropylene for improving heat resistance
and grease resistance; LDPE resins produced in a high-

35 pressure process; LLDPE resins produced by polymerising
ethylene and alpha-olefin comonomers in the presence of
a Ziegler, chromium or metallocene catalyst; and MDPE

resins.

In a preferred embodiment, the polymer is blended with LDPE, said LDPE preferably having a melt index of at least 3 g/10 min, preferably at least 6.5 g/10 min and being designed for extrusion coating. The LDPE may form 15 to 35 wt% of the final blend. The blend may be coated as a monolayer onto the substrate or it may be coextruded with other polymer(s) as is known in the art.

The substrate is preferably a fibre based material such as paper or cardboard. The substrate may also be a film made of, for example, polyester, cellophane, polyamide, polypropylene or oriented polypropylene. Other suitable substrates include aluminium foil.

The coating will typically be 10 to 1000 μm in thickness, especially 20 to 100 μm. The specific thickness will be selected according to the nature of the substrate and its expected subsequent handling conditions. The substrate may be as thick as 10 to 1000 μm, e.g. 6 to 300 μm.

Viewed from a further aspect the invention also provides a polyethylene composition for extrusion coating, said composition comprising a polyethylene produced by polymerization catalysed by a single site catalyst and having as comonomers to ethylene at least two C_{4-12} alpha olefins, preferably at least two alpha olefins selected from but-1-ene, hex-1-ene, 4-methyl-pent-1-ene, hept-1-ene, oct-1-ene, and dec-1-ene particularly but-1-ene and hex-1-ene.

Viewed from a further aspect the invention provides a process for extrusion coating a substrate comprising extruding a polyethylene produced by polymerization catalysed by a single site catalyst and which comprises as comonomers to ethylene at least two C_{4-12} alpha olefins, preferably at least two alpha olefins selected from but-1-ene, hex-1-ene, 4-methyl-pent-1-ene, hept-1-ene, oct-1-ene, and dec-1-ene particularly but-1-ene and hex-1-ene to form a polymer melt and coating a substrate

with said melt.

The extrusion coating of the invention preferably comprises either a bimodal terpolymer comprising

a)   a lower molecular weight copolymer of ethylene and but-1-ene

b)   a higher molecular weight copolymer of ethylene and a C_5 to C_{12} alpha-olefin (e.g. C_6 to C_{12} alpha-olefin)

or a bimodal polymer comprising

a)   a lower molecular weight polymer which is a binary copolymer of ethylene and a C_4 to C_{12} alpha-olefin and

b)   a higher molecular weight polymer which is either a binary copolymer of ethylene and but-1-ene, if the lower molecular weight polymer of a) is a binary copolymer of ethylene and a C_5 to C_{12} alpha-olefin(e.g. C_6 to C_{12} alpha-olefin), or a terpolymer of ethylene, but-1-ene and a C_5 to C_{12} alpha-olefin (e.g. C_6 to C_{12} alpha-olefin).

In a preferred embodiment the present invention provides a coating of a bimodal polymer with a relatively narrow molecular weight distribution (MWD) and excellent sealing properties, good processability, low water vapour permeability and a low level of extractibles. The MWD is preferably 2.5 to 10, especially 3.0 to 6.0.

The weight average molecular weight of the multimodal, e.g. bimodal polymer is preferably between 50,000 and 250,000 g/mol. The lower molecular weight polymer fraction preferably has a weight average molecular weight preferably of 5000 to 100,000 g/mol,

more preferably of 10,000 to 70,000 g/mol and the higher molecular weight polymer fraction preferably has a weight average molecular weight preferably of 50,000 to 500,000 g/mol, more preferably of 100,000 to 300,000 g/mol.

The molecular weight distribution of the polymer is further characterized by the way of its melt flow rate (MFR) according to ISO 1133 at 190°C. The final multimodal, e.g. bimodal polymer preferably has a melt flow rate MFR_2 of 1 to 30 g/10min, more preferably of 5 to 25 g/10min. The lower molecular weight polymer fraction preferably has a melt index MFR_2 of 5 to 1000 g/10min, more preferably of 10 to 200 g/10min.

The density of the polymer is preferably 905 to 940 kg/m^3, more preferably of 905 to 935 kg/m^3. The density of the lower molecular weight polymer fraction is preferably 920 to 950 kg/m^3, more preferably 925 to 940 kg/m^3. The density of the higher molecular weight component polymer fraction is preferably 880 to 910 kg/m^3, more preferably 895 to 905 kg/m^3. The lower molecular weight component should have a higher density than the higher molecular weight component.

The sealing initiation temperature can be controlled by adjusting the MFR of the polymer and the density of the lower molecular weight component. Higher MFR leads to lower seal initiation temperature. In a highly preferred embodiment the polymers of the invention give rise to a constant heat sealing force over a wide temperature range. Hence, the heat sealing force is substantially constant, e.g. the sealing force is within 2, preferably within 1 N/25.4mm , over a temperature range of at least 30°C, preferably at least 40°C. These properties are depicted in Figures 1 and 2.

The bimodal polymer according to the present invention preferably comprises 30 to 70%, more preferably 35 to 60% and most preferably 38 to 55% by weight of the lower molecular weight copolymer fraction

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with regard to the total composition.

The overall comonomer content in the polymer is preferably 0.5 to 10 mol%, preferably 1.5 to 6.5 mol%, more preferably 2 to 5 mol% and in the lower molecular

5   weight polymer the comonomer content is preferably from 0 to 2.0 mol%, preferably 0.5 to 1.5 mol%. In the higher molecular weight polymer the comonomer content is preferably 1.5 to 8 mol%, preferably 3.5 to 6 mol%. Comonomer contents may be measured by NMR.

10   The melting point of the polymer may be between 100 to 130°C, preferably 110 to 120°C.

Further, the molecular weight of the higher molecular weight copolymer fraction should be such that when the lower molecular weight copolymer fraction has

15   the melt index and density specified above, the final bimodal polymer has the melt index and density as discussed above.

In addition to the polymer itself, the coating of the invention may also contain antioxidants, process

20   stabilizers, pigments and other additives known in the art. Moreover, the multimodal single site catalyst ethylene polymer with two other alpha-olefin comonomers may be blended with other polymers while retaining sealing and mechanical properties suitable for the

25   desired end-uses. Examples of such further polymers which may be used include LDPE, HDPE, MDPE, LLDPE, EMA, EBA, and EVA. Typically, up to about 50% wt of the overall polymer may be constituted by much further polymers, more preferably up to 30% wt in the case of

30   HDPE, MDPE or LLDPE. The multimodal single site catalyst ethylene polymer with two other alpha-olefin comonomers may also be used to produce films on a cast film line.

The present invention will now be illustrated

35   further by the following non-limiting Examples and the accompanying Figures which show the heat sealing properties of various of the examples.

Experimental:

Melt flow rate (MFR, sometimes also referred to as
melt index) according to ISO 1133, at 190°C. The load
used in the measurement is indicated as a subscript,
i.e. MFR_2 denotes the MFR measured under 2.16 kg load.

Molecular weight averages and molecular weight
distribution were determined by size exclusion
chromatography (SEC) using Waters Alliance GPCV2000
instrument with on-line viscometer. Oven temperature was
140 °C. Trichlorobenzene was used as a solvent.

Density was determined according to ISO 1183-1987.

But-1-ene and hex-1-ene contents of the polymers
were determined by ^{13}C NMR.

Basis weight was determined as follows: Five samples
were cut off from the extrusion coated paper parallel in
the transverse direction of the line. The size of the
samples was 10 cm x 10 cm. The samples were put into a
solvent for 10 - 30 minutes, after which the paper was
removed from the plastic and the solvent was allowed to
evaporate. The samples were then weighed and the average
was calculated. The result was given as a weight of the
plastic per square meter.

If the paper substrate had a uniform basis weight,
then the measurement could be done without removing the
paper. In such a case the basis weight of the paper was
subtracted from the measured basis weight. The
difference was reported as the result.

Rheology of the polymers was determined using
Rheometrics RDA II Dynamic Rheometer. The measurements
were carried out at 190°C under nitrogen atmosphere. The
measurements gave storage modulus (G') and loss modulus
(G'') together with absolute value of complex viscosity
(η^*) as a function of frequency (ω) or absolute value of
complex modulus (G*).

$$\eta^* = \sqrt{(G'^2 + G''^2)}/\omega$$

$$G^* = \sqrt{(G'^2 + G''^2)}$$

5

According to Cox-Merz rule complex viscosity function, $\eta^*(\omega)$ is the same as conventional viscosity function (viscosity as a function of shear rate), if frequency is taken in rad/s. If this empirical equation

10 is valid absolute value of complex modulus corresponds shear stress in conventional (that is steady state) viscosity measurements. This means that function $\eta^*(G^*)$ is the same as viscosity as a function of shear stress.
In the present method both viscosity at a low shear

15 stress or η^* at a low G^* (which serve as an approximation of so called zero viscosity) and zero shear rate viscosity were used as a measure of average molecular weight. On the other hand, shear thinning, that is the decrease of viscosity with G^*, gets more

20 pronounced the broader is the molecular weight distribution. This property can be approximated by defining a so-called shear thinning index, SHI, as a ratio of viscosities at two different shear stresses. In the examples below the shear stresses (or G^*) 0 and 100

25 kPa were used. Thus:

$$SHI_{0/100} = \eta^*_0/\eta^*_{100}$$

where

30 η^*_0 is the zero shear rate viscosity
η^*_{100} is complex viscosity at $G^* = 100$ kPa

As mentioned above storage modulus function, $G'(\omega)$, and loss modulus function, $G''(\omega)$, were obtained as

35 primary functions from dynamic measurements. The value

of the storage modulus at a specific value of loss modulus increases with broadness of molecular weight distribution. However this quantity is highly dependent on the shape of molecular weight distribution of the polymer. In the examples the value of G' at G'' = 5 kPa was used.

Melting temperature and crystallinity was determined by differential scanning calorimetry (DSC) using Mettler Toledo DSC822, with heating and cooling rate of 10°C/min.

Catalyst Preparation Example 1:

134 grams of a metallocene complex (bis (n-butyldicyclopentadienyl) hafnium dichloride supplied by Witco as TA02823, containing 0.36 % by weight Hf) and 9.67 kg of a 30% solution of methylalumoxane (MAO) in toluene (supplied by Albemarle) were combined and 3.18 kg dry, purified toluene was added. The thus obtained complex solution was added on 17 kg silica carrier Sylopol 55 SJ by Grace. The complex was fed very slowly with uniform spraying during 2 hours. Temperature was kept below 30°C. The mixture was allowed to react for 3 hours after complex addition at 30°C. The thus obtained solid catalyst was dried by purging it with nitrogen at 50°C for three hours and recovered.

Catalyst Preparation Example 2:

Benzylation of (n-BuCp)$_2$HfCl$_2$ by using benzyl potassium
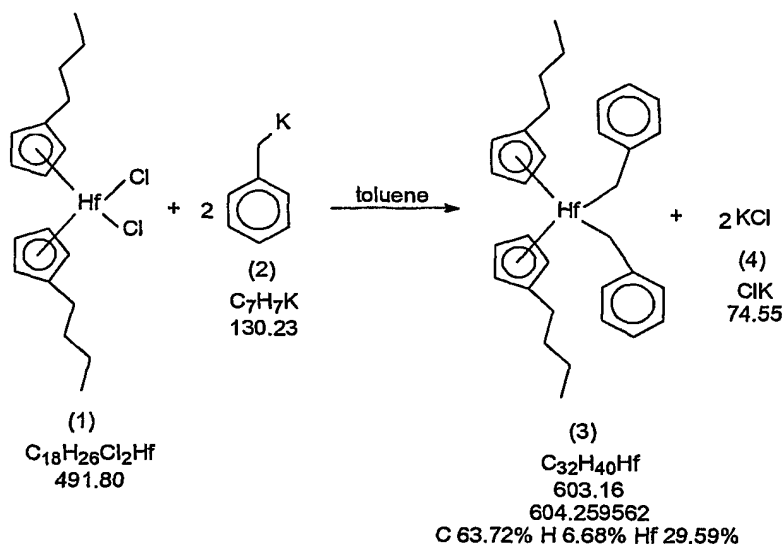*Synthesis of benzyl potassium*
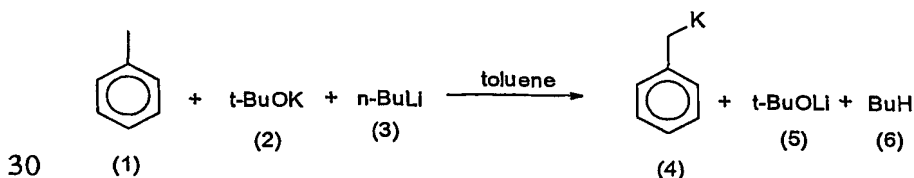
First, 200 mmol of potassium tert-butoxide (Fluka 60100, 97%) was dissolved in 250 ml toluene. Next, 200 mmol of

n-butyllithium (~2.5 M solution in hexanes, Aldrich) was added during 1.5 hours. The mixture turned from white into red. The mixture was stirred for 2.5 days. It was then filtrated and washed with toluene (5x100 ml) and
5   pentane (50 ml). As a result 21.7 grams benzylpotassium was obtained as brick red, toluene insoluble solid. Yield was 83%.

^{1}H-NMR in THF-d$_8$, δ(ppm): 6.01 (m, 2H), 5.10 (d, 2H),
10 4.68 (t, 1H), 2.22 (s, 2H). Chemical shifts are referenced to the solvent signal at 3.60 ppm. ^{13}C-NMR in THF-d$_8$, δ(ppm): 152.3, 129.4, 110.1, 94.3, 51.6. Chemical shifts are referenced to the solvent signal at 66.50 (the middle peak).

15

<u>Synthesis of (n-BuCp)$_2$Hf(CH$_2$Ph)$_2$</u>

(1)
C$_{18}$H$_{26}$Cl$_2$Hf
491.80

(2)
C$_7$H$_7$K
130.23

(3)
C$_{32}$H$_{40}$Hf
603.16
604.259562
C 63.72% H 6.68% Hf 29.59%

(4)
ClK
74.55

20 6.87 mmol bis(n-butylcyclopentadienyl)hafnium dichloride and 150 ml of toluene were mixed at 20°C to give brown-grey solution. Then, 14.74 mmol of benzylpotassium prepared as described above was added to the solution at 0°C as a solid during 10 minutes. The cooling bath was
25 removed and the mixture was stirred at 20°C for 3 hours.

Solvent was removed under reduced pressure and the remainder was extracted with 3 x 30 ml of pentane. The solvent was removed from the combined pentane solutions giving 3.86 g of (n-BuCp)$_2$Hf(CH$_2$Ph)$_2$ as a yellow liquid. Yield 93%.

^{1}H-NMR in toluene-d$_8$, δ(ppm): 7.44 (t, 4H), 7.11 (d, 4H), 7.08 (t, 2H), 5.75 (m, 4H), 5.67 (m, 4H), 2.33 (t, 4H), 1.77 (s, 4H), 1.54 (m, 4H), 1.43 (m, 4H), 1.07 (t, 6H). Chemical shifts are referenced to the solvent signal at 2.30 ppm (the middle peak). ^{13}C-NMR in toluene-d$_8$, δ(ppm): 152.7, 137.5, 128, 126.8, 121.6, 112.7, 110.5, 65.3, 34.5, 29.7, 22.8, 14.1. Chemical shifts are referenced to the solvent signal at 20.46 (the middle peak). Elemental analysis[1]: C 63.57% (calc. 63.72), H 6.79% (calc. 6.68), Hf 29.78% (calc. 29.59), K <0.1% (calc. 0).

Catalyst Support and Activation

The metallocene was supported and activated as in Catalyst Preparation Example 1, except that the 134 grams of (n-BuCp)$_2$HfCl$_2$ was replaced by 164 grams of (n-BuCp)$_2$Hf(CH$_2$Ph)$_2$ prepared as described above and as the silica carrier SP9-391 (supplied by Grace) was used.

Example 1:

A continuously operating loop reactor having a volume of 500 dm^3 was operated at 85°C temperature and 60 bar pressure. Into the reactor were introduced propane diluent, ethylene, but-1-ene comonomer, hydrogen and the polymerisation catalyst prepared according to Catalyst Preparation Example 1 in such amounts that the ethylene concentration in the liquid phase of the loop reactor was 7% by mol, the ratio of hydrogen to ethylene was 0.65 mol/kmol, the ratio of but-1-ene to ethylene was 155 mol/kmol and the polymer production rate in the

reactor was 25 kg/h. The thus formed polymer had a melt
index MFR_2 of 100 g/10 min and a density of 935 kg/m^3.

The slurry was intermittently withdrawn from the
reactor by using a settling leg and directed to a flash
tank operated at a temperature of about 50°C and a
pressure of about 3 bar.

From the flash tank the powder, containing a small
amount of residual hydrocarbons, was transferred into a
gas phase reactor operated at 75°C temperature and 20
bar pressure. Into the gas phase reactor were also
introduced additional ethylene, hex-1-ene comonomer and
nitrogen as inert gas in such amounts that the ethylene
concentration in the circulating gas was 22% by mole,
the ratio of hydrogen to ethylene was about 0.5
mol/kmol, the ratio of hex-1-ene to ethylene was 12
mol/kmol and the polymer production rate was 26 kg/h.
The concentration of but-1-ene was so low that it could
not be detected by the on-line gas chromatograph which
was used to monitor the gas composition.

The polymer collected from the gas phase reactor was
stabilised by adding to the powder 400 ppm Irganox B561.
The stabilised polymer was then extruded and pelletised
under nitrogen atmosphere with a CIM90P extruder,
manufactured by Japan Steel Works. The melt temperature
was 200°C, throughput 280 kg/h and the specific energy
input (SEI) was 200 kWh/t.

The production split between the loop and gas phase
reactors was thus 49/51. The polymer pellets had a melt
index MFR_2 of 2.7 g/10 min, a density of 920 kg/m^3, a
but-1-ene content of 2.1% by weight, a content of hex-1-
ene of 6.3% by weight, a weight average molecular weight
M_w of 90600 g/mol, a number average molecular weight M_n
of 16200 g/mol and a z- average molecular weight M_z of
226000 g/mol. Further, the polymer had a zero shear rate
viscosity η_0 of 3630 Pa·s, a shear thinning index $SHI_{0/100}$
of 4.1.

Example 2:

The procedure of Example 1 was repeated except that the process conditions were adjusted as shown in Table 1. The polymer properties are shown in Table 2.

5

Example 3:

The procedure of Example 1 was repeated except that the process conditions were adjusted as shown in Table 1. The polymer properties are shown in Table 2.

10

Example 4:

The procedure of Example 1 was repeated except that the process conditions were adjusted as shown in Table 1. The polymer was not pelletised but it was collected as

15   powder. The polymer properties are shown in Table 2.

Example 5:

The procedure of Example 4 was repeated except that the process conditions were adjusted as shown in Table 1.

20   Before the powder was pelletised, into the polymer was added 15 %CA8200, which is an LDPE polymer for extrusion coating, manufactured and marketed by Borealis having an MFR$_2$ of 7.5 g/10 min and density 920 kg/m^3. The polymer properties shown in Table 2 are determined from the

25   powder.

Example 6:

The procedure of Example 1 was repeated except that the catalyst was prepared according to Catalyst Preparation

30   Example 2 and that the process conditions were adjusted as indicated in Table 1. The resulting powder was then dry blended with 12% of CA8200 and extruded as described in Example 1. The analysis data is given in Table 2. The molecular weights, crystallinity and the comonomer

35   contents were measured from the powder, while the rheological properties were measured from the blend.

Example 7:

The procedure of Example 6 was repeated except that the
process conditions were adjusted as indicated in Table
5 1. No LDPE was added to the polymer. The analysis data
is given in Table 2.

Example 8:

The procedure of Example 6 was repeated except that the
10 process conditions were adjusted as indicated in Table
1. A part of the powder was then recovered and extruded
as described in Example 1. No LDPE was added to the
polymer. The analysis data is given in Table 2.

15 **Example 9:**

The procedure of Example 6 was repeated except that the
process conditions were adjusted as indicated in Table
1. Further, a part of the resulting powder was recovered
and dry blended with 9 % of CA8200 and then extruded as
20 described in Example 6. The analysis data of the blend
is given in Table 2.

Example 10:

A part of the powder of Example 8 was dry blended with
25 13% of CA8200 and then extruded as described in Example
6. The analysis data of the blend is given in Table 2.

Example 11:

A part of the powder of Example 8 was dry blended with
30 24% of CA8200 and then extruded as described in Example
6. The analysis data of the blend is given in Table 2.

Example 12

The procedure of Example 6 was repeated, except that the
35 temperature in the gas phase reactor was 80 °C, the
operating conditions were otherwise as indicated in

Table 1 and the amount of LDPE was 10 % by weight. The polymer analysis data is given in Table 2. The molecular weights, crystallinity and the comonomer contents were measured from the powder, while the rheological

5 properties were measured from the blend.

Example 13:

The procedure of Example 12 was repeated, except that the operating conditions were as indicated in Table 1

10 and the amount of LDPE was 25 % by weight. The polymer analysis data is given in Table 2. The molecular weights, crystallinity and the comonomer contents were measured from the powder, while the rheological properties were measured from the blend.

15

Example 14:

The procedure of Example 12 was repeated, except that the operating conditions were as indicated in Table 1 and the amount of LDPE was 30 % by weight. The polymer

20 analysis data is given in Table 2. The molecular weights, crystallinity and the comonomer contents were measured from the powder, while the rheological properties were measured from the blend.

Table 1: Polymerisation reactor conditions

Example	1	2	3	4	5	6	7	8	9
$C_2^=$ loop, mol%	7	7	7.2	7.2	6.5	6.0	5.3	6.7	6.8
H_2/C_2 loop, mol/kmol	0.65	0.63	0.63	0.64	0.59	0.5	0.42	0.38	0.36
C_4/C_2 loop, mol/kmol	155	160	155	160	175	105	200	165	180
C_6/C_2 loop, mol/kmol	0	0	0	0	0	0	0	0	0
MFR_2 loop, g/10 min	100	100	120	130	100	108	109	39	35
Density loop polymer, kg/m³	935	935	936	936	937	938	936	932	931
Productn rate loop, kg/h	25	29	30	27	31				
$C_2^=$ in gpr, mol%	25	23	19	20	21	48	49	53	58
H_2/C_2 in gpr, mol/kmol	0.4	0.5	1.0	1.3	0.6	0.9	0.4	0.9	0.9
C_4/C_2 gpr, mol/kmol	*	*	*	*	*	*	*	*	*
C_6/C_2 gpr, mol/kmol	12	12	12	13	11	12	10	12	12
Productn rate in gpr, kg/h	26	30	30	27	31				
Prodctn split, Loop/gpr	49/ 51	49/ 51	50/ 50	50/ 50	50/ 50	50/ 50	50/ 50	50/ 50	50/ 50

* indicates that the level was too low to be detected by GC

5

Table 1 cont

Example	12	13	14
$C_2^=$ in loop, mol-%	7.3	7.2	7.5
H_2/C_2 in loop, mol/kmol	0.54	0.50	0.52
C_4/C_2 in loop, mol/kmol	146	156	147
C_6/C_2 in loop, mol/kmol	0	0	0
MFR_2 of loop polymer, g/10 min	140	90	110
Density of loop polymer, kg/m^3	934	936	934
Production rate in loop, kg/h			
$C_2^=$ in gpr, mol-%	47	33	51
H_2/C_2 in gpr, mol/kmol	1.2	1.4	1.1
C_4/C_2 in gpr, mol/kmol	*	*	*
C_6/C_2 in gpr, mol/kmol	19	17.5	14
Production rate in gpr, kg/h			
Production split, Loop/gpr	51/49	51/49	53/47

Table 2: Polymer properties

Example	1	2	3	4	5	6
MFR_2, g/10 min	2.7	3.8	20	9.0	14	16
Density, kg/m^3	920	916	915	915	915	918
M_z/1000	226	197	134	182	143	N.D.
M_w/1000	90.6	84.7	59.6	78	71.7	N.D.
M_n/1000	16.2	20	16.9	21.7	21.7	N.D.
η_0, Pa·s	3630	2380	460	1020	540	732
$SHI_{0/100}$	4.1	3.7	2.7	3.5	2.9	3.9
η_1, Pa·s	3430	2290	440	970	500	660
$SHI_{1/100}$	3.9	3.5	2.6	3.3	2.7	3.5
G'_{5kPa}, Pa	1030	950	810	970	850	1130
T_m, °C	117.8	117.6	117.3	117.3	117.4	118
Crystallinity,%	42.1	37.1	36.7	36.4	27.6	N.D.
but-1-ene, wt-%	2.1	2.0	N.D.	2.1	2.1	N.D.
hex-1-ene, wt-%	6.3	8.3	N.D.	9.5	8.7	N.D.
LDPE, wt-%	0	0	0	0	15	12

Table 2 cont

Example	7	8	9	10	11	12	13	14
MFR_2, g/10 min	4.9	11	11	11	11	8.8	13	10
Density, kg/m^3	920	918	918	919	919	919	918	920
M_z/1000	N.D.	140	N.D.	N.D.	N.D.	282	693	1425
M_w/1000	N.D.	68.7	N.D.	N.D.	N.D.	98.5	118	171
M_n/1000	N.D.	19.6	N.D.	N.D.	N.D.	23.5	20.3	19
η_0, Pa·s	2357	785	570	959	816	1117	840	1214
$SHI_{0/100}$	4.9	2.2	2	3.1	2.7	3.6	4.4	5.9
η_1, Pa·s	2120	760	550	870	760	1030	740	1000
$SHI_{1/100}$	4.5	2.2	2	2.8	2.5	3.4	3.8	4.9
G'_{5kPa}, Pa	1260	610	520	930	820	1020	1270	1480
T_m, °C	N.D.	116.3	115.6	115.8	115.2	115.7	116.1	115.3
Crystallinity%	N.D.	37.7	N.D.	N.D.	N.D.	37.7	38.1	38.5
but-1-ene, wt%	N.D.	2.2	N.D.	N.D.	N.D.	2.0	N.D.	N.D.
hex-1-ene, wt%	N.D.	7.8	N.D.	N.D.	N.D.	8.1	N.D.	N.D.
LDPE, wt-%	0	0	9	13	24	10	25	30

N.D. indicates that the property was not determined for
the respective sample

5   **Comparative Example 1:**

The polymer manufactured and sold by Dow under trade
name Affinity PT1451 was used in the coating
experiments.

10   **Comparative Example 2:**

The polymer manufactured and sold by Borealis under
trade name CA8200 was used in the coating experiments.
The polymer had MFR_2 of 7.5 g/10 min and density of 920
kg/m^3.

15

Comparative Example 3

(made according to WO 02/02323):
A continuously operating loop reactor having a volume of
500 dm^3 was operated at 85°C temperature and 60 bar
20   pressure. Into the reactor were introduced propane
diluent, ethylene, but-1-ene comonomer, hydrogen and the
polymerisation catalyst prepared according to Catalyst
Preparation Example 1 in such amounts that the ethylene
concentration in the liquid phase of the loop reactor
25   was 6.6 % by mole, the ratio of hydrogen to ethylene was
0.63 mol/kmol, the ratio of but-1-ene to ethylene was
183 mol/kmol and the polymer production rate in the
reactor was 25 kg/h. The thus formed polymer had a melt
index MFR_2 of 120 g/10 min and a density of 936 kg/m^3.
30   The slurry was intermittently withdrawn from the
reactor by using a settling leg and directed to a flash
tank operated at a temperature of about 50°C and a
pressure of about 3 bar.
         From the flash tank the powder, containing a small
35   amount of residual hydrocarbons, was transferred into a
gas phase reactor operated at 75 °C temperature and 20
bar pressure. Into the gas phase reactor were also

26

introduced additional ethylene, but-1-ene comonomer and
nitrogen as inert gas in such amounts that the ethylene
concentration in the circulating gas was 23 % by mole,
the ratio of hydrogen to ethylene was about 1.2

5   mol/kmol, the ratio of but-1-ene to ethylene was 48
mol/kmol and the polymer production rate was 26 kg/h.
The production split was thus 49/51. No hex-1-ene was
introduced into the gas phase reactor.

The polymer collected from the gas phase reactor was

10   stabilised by adding to the powder 400 ppm Irganox B561.
The stabilised polymer was then extruded and pelletised
under nitrogen atmosphere with a CIM90P extruder,
manufactured by Japan Steel Works. The melt temperature
was 200°C, throughput 280 kg/h and the specific energy

15   input (SEI) was 200 kWh/t.

The production split between the loop and gas phase
reactors was thus 49/51. The polymer pellets had a melt
index MFR_2 of 10 g/10 min, a density of 916 kg/m^3, a but-
1-ene content of 8.1 % by weight, a weight average

20   molecular weight M_w of 67800 g/mol, a number average
molecular weight M_n of 19600 g/mol and a z- average
molecular weight M_z of 140000 g/mol. Further, the polymer
had a zero shear rate viscosity η_0 of 800 Pa·s, a shear
thinning index $SHI_{0/100}$ of 2.4.

25

Example 15:

The polymer powder produced in Example 4 was dry blended
with CA8200 and Irganox B561 so that the amount of
CA8200 was 15% by weight and the amount of Irganox B561

30   was 400 ppm of the total composition. The resulting
blend was extruded and pelletised under nitrogen
atmosphere using Berstorff BZE40A extruder so that the
throughput was 40 kg/h and melt temperature 195°C.

35   **Example 16:**

Extrusion coating runs were made on Beloit coextrusion
coating line. It had a Peter Cloeren's die and a five

layer feed block. The width of the line was 850 - 1000
mm and the maximum line speed was 1000 m/min (design
value).

In the coating line above a UG kraft paper having a
5   basis weight of 70 g/m² was coated with a layer of CA8200
having a basis weight of 6 g/m² and a layer of inventive
polymer composition prepared in Examples 1 to 9 having a
basis weight of 26 g/m². The temperature of the polymer
melt was set to 300°C. The line speed was 100 m/min.
10

Example 17:

Extrusion coating runs were made according to Example
16, except that monolayer coatings were produced at
different line speeds. The highest line speed showing a
15 stable behaviour was reported.

Monolayer coatings were made from the materials so
that the basis weight was 10 g/m². The data is shown in
Table 3.

20 Table 3:

Product of Example	Maxrpm	Max line speed DD (mono) m/min	Coating weight (mono) g/m²
3	243	no	no
4	199	no	no
5	212	>500	10,1-11,3
C.E.1	127	>500	
C.E.2	>250	>500	
6	240	>500	10,0-10,5
7	137	>500	10,0-11,0
8	116	no	no
9	131	>500	9,2-10.9
10	127	>500	10,2-12,0
11	145	>500	10,9-12,4
12	164	500	10.3-11.0
13	219	>500	10.5-11.9
14	204	>500	10.8-11.9

"no" means that at line speed of more than 400 m/min the
behaviour was so unstable that the coating could not be
analysed. N.D. indicates that the property was not
5   determined for the respective sample.

The column maxrpm indicates the maximum RPM value of the
extruder motor when preparing the coating. The higher
the value, the better is the processability and the
10   higher is the throughput of the polymer.
        The column max line speed indicates the maximum line
speed of the web in m/min. A low maximum line speed
indicates that the resin has a tendency to undergo draw
resonance, where the polymer flow from the die starts to
15   oscillate heavily and causes the coating to become
uneven. The higher the value, the better is the
performance of the polymer on the coating line and the
production rate of coating is higher.
        The column coating weight shows the measured coating
20   weight and the range where it varied. The conditions
were not optimised to minimise the variation.

Example 18:
The coatings produced in Example 16 were put to a hot
25   tack test to measure the sealability. The sample (coated
side against coated side) was folded and pressed
together at an elevated temperature. The sealing time
was 0.5 seconds, the lag time was 0.2 seconds and the
sealing pressure was 1.5 N/mm^2 for a specimen width of 15
30   mm. The force to break the seal was then measured. The
data is shown in the attached figure.

Discussion:

35   From the Examples and Comparative Examples it can be
seen that:

- the polymer of Comparative Example 1 has extremely good sealing properties; however, it has a poor processability as indicated by the low maximum RPM value in Table 3

5 - the polymer of Comparative Example 2 has poor sealing properties; however, it has extremely good processability

- the polymers of the Examples 1 to 14 have a combination between good sealing properties and

10   processability.